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Chemical erosion of pyrolytic graphite by low-energy H^+ and D^+ impact

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Abstract

Recent developments have lead to prospects of lower plasma edge temperatures in the divertor region of tokamaks and, consequently, a growing interest in the interaction of graphite with low-energy hydrogen ions (10s of eV). Here we present experimental measurements of methane and heavier hydrocarbon yields of pyrolytic graphite (300 K-1000 K temperature) for H^+ impact energies of 10-200 eV. Heavier hydrocarbons contribute significantly to the total chemical erosion yield at low energies. Comparison of CH_4 yields due to H^+ irradiation of graphite with similar results for CD_4 yields due to D^+ shows a smaller isotopic effect than anticipated based on previous H^+ and D^+ measurements. Comparisons are also made between the experimental results and a recently proposed model.

Keywords: Chemical erosion; Low-Z wall material; Plasma wall interaction; Graphite

1. Introduction

Carbon-based materials are among fusion plasma facing candidates because of their low Z and excellent thermo-mechanical properties. Such materials, however, are susceptible to erosion under plasma particle bombardment by both physical and chemical processes, reducing component lifetimes and increasing impurities in the plasma. In particular, under hydrogen ion and atom irradiation, the erosion of carbon is enhanced at temperatures between 300 and 1000 K due to the formation of volatile hydrocarbon molecules producing maximum yields more than 10 times greater than those due to physical sputtering alone [1].

Many studies of the chemical erosion of graphite by energetic hydrogen ions in the energy range of 100 eV-3 keV have been conducted and reviews of these results are available [2,3]. Briefly, the chemical erosion of graphite under energetic hydrogen bombardment is characterized by a pronounced temperature dependence with hydrocarbon yield maxima (Y_m) occurring between 725-825 K (T_m). The absolute magnitude of Y_m also depends on the ion energy and flux [4]. Nuclear energy deposition, in the form of broken carbon bonds [5], and volatile molecule formation at the end of the ion range (following thermalization) [6-8] play key roles in explaining the observed features [2].

As the energy of the impacting hydrogen ions is decreased, the relative contributions of the heavier hydrocarbons C_2H_x and C_3H_y to the total erosion yield become significant [9,10]. Whereas methane comprises 90% of the total yield for 3 keV H^+ impact at T_m, it represents about 50% of the C-yield at 50 eV [9,11] and only 5-10% of the C-yield for thermal H atom impact [9,12]. Some discrepancies exist in these studies with regard to the magnitude of the C_2H_x contributions. Yamada found that the contribution from these heavier hydrocarbons eclipsed that due to methane for energies < 1 keV [10] and later attributed some of the discrepancy to a fluence effect on heavy hydrocarbon formation [13].

Recently, prospects of lower plasma edge temperatures in the divertor region of tokamaks have shifted the research focus towards the interaction of graphite with hydrogen ions of 10s of eV energy. Laboratory studies indicate that the methane yield dependence on temperature

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broadens as the ion energy is reduced such that significant erosion occurs even at room temperature for energies below about 100 eV [14–16]. Roth and Bohdansky [14] reported the yield at room temperature to be nearly independent of ion energy for energies between 30 and 80 eV. More recently, this energy range has been extended down to 10 eV for D^+ impact and the methane yield was found to decrease as the energy decreases below ~ 50 eV [16].

A remarkable feature of the observed low-energy chemical erosion is that it occurs for hydrogen energies below the threshold (~ 40 eV for H^+ and 33 eV for D^+ [17]) for physical sputtering of carbon and thus precludes the role of damage deposition used to explain the high energy results. The results of Davis et al. [9] and Wu et al. [18] show significant changes in Y_m, T_m, and activation energies as ion energies decrease below ~ 100 eV, indicating a change in the dominating reaction mechanism(s). However, isotopic evidence [14] and thermal desorption spectroscopy results [15] suggest that ion energy still plays a role in these near-surface reactions, although no threshold has been observed down to 10 eV [15,16].

Efforts have been made recently to model this near-surface erosion of graphite with a semi-empirical formula which is similar to that used for physical sputtering, but which utilizes a much lower threshold energy of 1–2 eV [19]. The contribution of this term to the total yield is restricted to ion energies below 90 eV. Our new experimental results will enable comparisons to be made with model predictions.

2. Experiment

All experiments were performed in an ultra-high vacuum facility (pumped by a 360 L/s Leybold turbo molecular pump) with base pressures of $< 10^{-9}$ Torr after baking the whole system at 500 K. The facility is equipped with a Specs IQE 12/38 electron-impact ion source and a Wien-type mass filter so that mass selected beams of D_2^+ and H_3^+ are transmitted through a five-element electrostatic deceleration lens onto the test specimen. The computer code ''MacSimion'' was used to calculate ion trajectories in order to determine the correct voltages to apply to the axially symmetric deceleration lens elements. The resulting ion beam has been profiled and spot sizes of ~ 0.12 cm^2 were achieved for deceleration to 10 eV/atom (i.e., based on 3 H atoms/H_3^+ and 2 D atoms/D_2^+). In this paper we refer to the incident beam particles as H^+ or D^+ even though not all of the atoms in the molecular ion are charged. It is recognized that when the low-energy molecular ions break up, upon striking the surface, there may be an uneven sharing of energy between the atoms, on the order of the molecular binding energy, a few eV [16]. It is also possible that the atoms in the molecular ion do not act independently as they interact with the surface atoms, and this may affect the hydrocarbon formation process [16]. Ion impact on the specimen was at normal incidence with a flux density of $\sim 1 \times 10^{18}$ H^+/m^2s or 3×10^{18} D^+/m^2s for all ion energies. The beam intensity was measured on the specimen which was biased to a high positive voltage (570 V in the case of 30 eV H_3^+ impact) suppressing secondary electron emission. Specimen temperature variation was achieved by resistive heating, and the temperature was measured by optical pyrometry.

A single specimen was used for all experiments. It was made of pyrolytic graphite (Union Carbide HPG99) in the form of a strip of dimensions $40 \times 10 \times 0.1$ mm^3. Following exposure to air, the specimen was baked at 1100 K for 12 h. Annealing at 1900 K for 30 s was performed between experiments of different ion energies in order to remove ion-induced damage due to prior irradiation.

The hydrocarbon products were monitored in the residual gas using an Extranuclear quadrupole mass spectrometer (QMS). The QMS sensitivity for CH_4 and C_3H_6 was calibrated in situ using known leaks, while the QMS sensitivities for the other reaction products (C_2H_2, C_2H_4,C_2H_6, C_3H_8), as well as their cracking patterns, were inferred from previous calibrations using the same QMS [9]. The erosion product spectrum analysis was accomplished using a technique similar to that described by Davis et al. [9].

Corrections for the wall contribution from the reflected beam particles were made by assuming that the QMS signals resulting from an incident H^+ or D^+ beam on the specimen immediately after annealing were due to wall effects, while hydrocarbon production from the specimen increased gradually thereafter, with a time constant of ~ 1 min. (fluences of $\sim 10^{20}$ D, H/m^2). These background levels were similar to those found by bombarding the specimen at 1100 K, where chemical activity is expected to be very low. It should be noted that where calculated specimen yields are small ($< 10^{-3}$ molecule/H^+) small errors in the wall contribution can lead to large relative errors in the yields.

3. Results and discussion

3.1. Temperature dependence

Chemical erosion experiments have been performed for H^+ ion energies between 10 and 200 eV/H^+. The temperature dependence of the total chemical erosion yield [i.e. C_{chem}/H^+] for six different energies ranging from 10 eV to 200 eV is shown in Fig. 1a. The remainder of Fig. 1 shows the methane and heavier hydrocarbon yields, for 200, 50 and 10 eV energies. In Fig. 1a, the total yield curve for 200 eV shows the most peaked profile with a maximum yield of 5.1×10^{-2} C/H^+ at 690 K. Broadening of the profiles as the energy is reduced results in increased yields at lower temperatures. In fact, the 50 eV and 25 eV curves nearly coincide with a maximum of

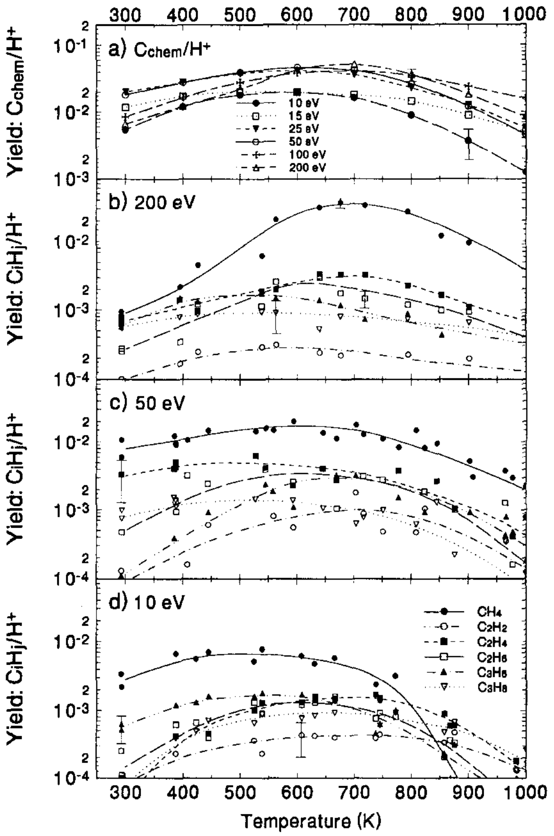

Fig. 1. (a) Total chemical erosion, and (b–d) hydrocarbon yields of pyrolytic graphite due to H^+ impact as a function of specimen temperature for various incident energies. The legend in (d) also applies to (b) and (c). The lines through the data serve to aid the reader. For all figures in this paper, C_{chem} is the total number of C-atoms measured in the form of hydrocarbons, i.e. $C_{chem} = CH_4 + 2(C_2H_2 + C_2H_4 + C_2H_6) + 3(C_3H_6 + C_3H_8)$.

4.2×10^{-2} C/H^+ at 600 K which is reduced only by a factor of 2 at 300 K. Between 25 and 10 eV, however, there is a downward shift in the yield at all temperatures so that the yields at 10 eV are consistently 2–3 times smaller than those for 25 eV.

For the methane yield (Fig. 1b–d), again the most peaked profile is seen for 200 eV, with a maximum yield of $\sim 3.4 \times 10^{-2}$ CH_4/H^+ at 700 K. As the energy is reduced, the profiles at the low-temperature end broaden and both Y_m and T_m shift downwards so that, at 10 eV, a maximum methane yield of $\sim 6.6 \times 10^{-3}$ CH_4/H^+ is observed at ~ 500 K.

The contributions of heavier hydrocarbon species to the total chemical erosion yield are also temperature dependent and, in general, become more significant as the ion energy is reduced; see Fig. 1. For example, in the region of T_m, methane comprises ~ 70% of the total yield for 200 eV impact, but just ~ 30% at 10 eV.

3.2. Energy dependence

In Fig. 2 the methane and total chemical yields from the present experiment are plotted as a function of H^+ energy for selected temperatures. At 300 K the methane yield exhibits a peak at ~ 50 eV (8×10^{-3} CH_4/H^+) and decreases as the energy is reduced (3×10^{-3} CH_4/H^+ at 10 eV), suggesting that the yield is energy dependent at this temperature. A more nearly energy independent methane yield is observed at 500 K. For temperatures near the peak for methane yield due to energetic ion impact (~ 800 K for > 300 eV) a dramatic decrease in the methane yield of more than a factor of 20 is observed as the H^+ energy is decreased from 200 eV to 10 eV. This suggests that the 'high temperature' reaction channel, for CH_4 formation, dominating for high energy (> 300 eV impact) [2], is nearly suppressed at incident energies of 10s of eV. This effect is also observed at 1000 K. At these low

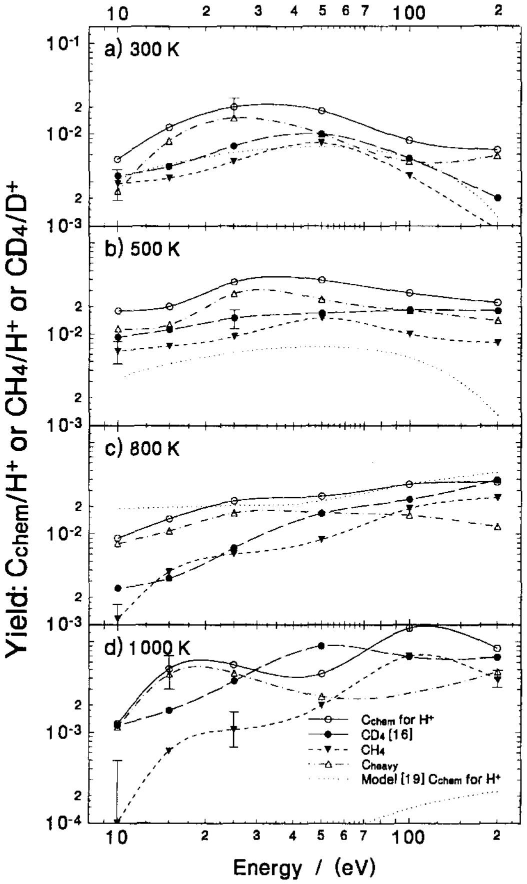

Fig. 2. Energy dependence of methane and total chemical erosion yields of pyrolytic graphite due to H^+ impact. The data are taken from the lines plotted in Fig. 1. CD_4 data [16] are shown for comparison, as are values calculated using a formula for the total chemical erosion of graphite in Ref. [19]: $C_{heavy} = C_{chem} - CH_4$. The legend in (d) applies to (a–c) also.

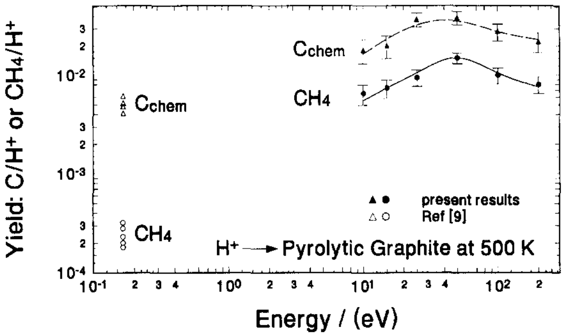

Fig. 3. Extension of methane and total chemical yields of pyrolytic graphite to sub-eV impact. Present data are taken from lines in Fig. 2b while sub-eV data are from Ref. [9].

energies another reaction channel appears to be occurring, consistent with the earlier observations of Davis et al. [9].

The total chemical yield curves as a function of H^+ impact energy (also presented in Fig. 2) follow the methane results, although the contributions from heavier hydrocarbons may shift the local yield maxima. At 300 K we again note the downward trend in yield for energies below 30 eV. At 800 K, however, the reduction in the total yield between 200 eV and 10 eV (factor of ~ 4) is much less pronounced than in the case of methane. Observing the C_{heavy}/H^+ curves in Fig. 2a–c, we note that the heavy hydrocarbon contribution appears to have a shallow maximum between 25 and 50 eV. Perhaps this is due to competing processes involving the formation of hydrocarbon surface complexes and the fragmentation of such complexes by the incident H_3^+.

The energy-dependence data for methane and C_{chem} in Fig. 2b are combined with previously published erosion yields for sub-eV atomic hydrogen impact on graphite at 500 K [9], in an attempt to identify the existence of any energy threshold; see Fig. 3. In the case of methane, the yield at 10 eV is still ~ 25 times that for thermal H atoms. For the total chemical yield the difference between 10 eV and thermal energies is only a factor of 3 or 4. Within the errors in the experiment, there is no clear evidence of an energy threshold in the energy range > 10 eV.

The formula of Roth and García-Rosales for the total chemical erosion due to H^+ ion impact [19] is also plotted in Fig. 2 for the flux used in our experiments, 10^{18} H^+/m^2s. The agreement with the present experimental results is good at 800 K. At 300 K, however, the predicted yields are significantly lower than those observed over the entire energy range. At 500 K the agreement becomes worse as the model predicts no change in the chemical yield while, experimentally, an increase is observed. At 1000 K the model severely underestimates the observed yields.

Previously obtained results for deutero-methane yields [16] are also shown in Fig. 2 for comparison. For temperatures up to 800 K both the CH_4 and CD_4 yields exhibit similar behavior. In general, for impact energies below 100 eV, the CH_4 yields are smaller than the CD_4 yields by less than a factor of two. This isotopic effect is somewhat smaller than the factor of five seen by Roth and Bohdansky for impact energies below 80 eV at room temperature [14]. The reason for this discrepancy is not evident.

4. Conclusions

The temperature dependence curves for the methane yield of pyrolytic graphite under H^+ impact broaden as the ion energy is decreased from 200 eV to 10 eV. This leads to significant yields at room temperature for ion energies as low as 10 eV. For methane, both Y_m and T_m decrease as the impact energy is reduced. The methane yields are also energy dependent and the nature of that dependence is a function of graphite temperature.

Heavier hydrocarbons contribute significantly to the total chemical yield as the ion energy is reduced, with a shallow maximum occurring near 25–50 eV. In general, the total chemical yield shows a similar behavior to that of methane but the contributions of heavy hydrocarbons tend to have a moderating effect on the observed dependencies.

The formula of Roth and García-Rosales agrees well with the observed total yield near 800 K but underestimates the yield at other temperatures. This discrepancy may partially be due to the near-surface energy deposition assumption based on an isotopic effect that is larger than we observed experimentally.

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